ABSTRACT

The crystals are an essential and fundamental component of the science and engineering of materials. In recent decades, interest in crystal growth processes has increased with increasing demand for materials for technological applications. For all solid-state applications, the study of crystalline materials has contributed greatly to the understanding of materials and has led to many advances in science and technology such as laser diode technology.

Nonlinear Optical (NLO) single crystals are capable of extending the available spectral region of laser radiation by the process of frequency conversion. The most important limitation to exploiting the potential of the photonic process is the difficulty of obtaining suitable material. It turns out that most available materials do not simultaneously meet the requirements for large and fast nonlinearity requirement for practical devices. It has been found that many organic and inorganic crystals are excellent optical materials. As crystal is a basic building block of a solid state material, growing newer and better crystals from existing is inevitably important. The desire to utilize the properties of these materials in applications such as telecommunications, optical data storage and optical information processing has created need for new materials with large second order susceptibilities. To enable a material to be potentially employable in NLO applications, the material should be in the bulk single crystal form.

The employability of single crystals in practical device applications has been impeded by their often inadequate transparency, poor optical quality and low laser damage threshold. Hence, new frequency conversion materials primarily concentrated on organic NLO materials with high nonlinear susceptibilities are to be explored. Amino acids containing amino (–NH_2) and the carboxylic acid (–COOH) functional group possess remarkable reactivity characteristics, due to which they can form several compounds in combination

with inorganic and organic reagents. Wide transparency in the visible and UV region along with molecular chirality, zwitterionic nature of the molecules and high damage thresholds create an interest in nonlinear amino acids. L–threonine ($C_4H_9NO_3$), a one of the promising polar amino acid with orthorhombic structure shows higher SHG efficiency.

The present work deals with spectroscopic investigations on L-threonine (LT) doped L-tartaric acid (TA), L-tartaric nicotinamide (LTN), thiourea (TU) single crystals were grown from solution growth technique for Nonlinear (NLO) applications.

The thesis consists of five chapters and as follows.

Chapter I devotes a brief introduction to various crystal growth methods with emphasis on low temperature solution growth and fundamental of nonlinear optics. The structural, elemental, optical and mechanical characterization techniques also presented in detail.

Chapter II presents the new single crystals of pure and 1 mol%, 3 mol% and 5 mol% of L-threonine doped tartaric acid (LT: TA), organic nonlinear optical materials were grown from their respective aqueous solution by slow evaporation method. The monoclinic crystalline nature of the grown crystals was confirmed by powder x-ray diffraction analysis (PXRD). Respective values of crystallite size (D), strain (Ɛ) and dislocation density (δ) have been calculated by using PXRD data. UV-Vis-NIR absorption and transmission spectra reveals the lower cut-off wavelength was around 281 nm and the crystals exhibit high transmission over visible and near IR region. The optical band gap is found to be 4.75, 4.28, 4.20 and 4.10 eV for pure, 1 mol%, 3 mol% and 5 mol% LT doped TA respectively. The presence of the functional groups such as O-H, C-H, C-O, C=O groups in the grown crystals were confirmed by Fourier Transform Infrared Spectroscopy (FTIR) analysis. CHN analysis was carried-out to confirm the presence of L-threonine in the grown crystals.

Micro-hardness study on the crystals revealed that the hardness number (H_v) was found to increase with the applied load. The growth pattern of the crystals were analysed through etching analysis from which the etch pattern were observed in the shape of 'step-triangle'. The second harmonic generation (SHG) property of pure and L-threonine doped tartaric acid crystals were confirmed by Kurtz-Perry powder technique.

Chapter III describes the new series of organic nonlinear optical single crystals of pure, 1 mol%, 3 mol% and 5 mol% L-threonine doped L-tartaric acid-nicotinamide (LTN) was synthesized and its single crystals were developed from their aqueous solution by a slow cooling method. The grown crystals with the sizes of 22 × 14 × 8 mm^3 (pure LTN), 25 × 12 × 9 mm^3 (1 mol% LT doped LTN), 19 × 9 × 9 mm^3 (3 mol% LT doped LTN) and 15 × 10 × 9 mm^3 (5 mol% LT doped LTN) were harvested. Powder X-ray Diffraction (PXRD) analysis shows that the grown crystals belong to the monoclinic crystal structure with the space group P_{21}. The crystallite size (D), strain (Ɛ) and dislocation density (δ) have been calculated by using PXRD data. L-threonine in grown crystals of LTN was confirmed by CHN analysis. The UV–Vis–NIR spectrum of pure and L-threonine doped LTN crystals indicates good transmission and less optical absorption over the entire visible range, allowing its potential use in optical applications. The optical band gap was calculated and found to be 4.03, 4.11, 4.15 and 4.22 eV for pure, 1 mol%, 3 mol% and 5 mol% of L-threonine doped LTN respectively. The vibrational mode of different molecular groups in pure and doped LTN single crystals was identified by FTIR spectral analysis. Micro-hardness study on the crystals revealed that the hardness number (H_v) was found to increase with the applied load. The growth pattern of the grown crystals were analysed through etching analysis at different etching durations (10 and 20 s), from which it is clear that the etch pit size was found to increase with an increase in the etching time. Second Harmonic Generation (SHG) property was confirmed by the Kurtz-Perry technique with the observation of emission of green light, when irradiated with 1064 nm fundamental of IR radiation.

Chapter IV focuses on the organic Nonlinear Optical (NLO) single crystals of pure and L-threonine Doped Thiourea (LTTU) were grown by slow evaporation technique at room temperature. The grown crystals belong to orthorhombic crystal system which was confirmed by powder XRD and also used to calculate crystallite size, strain and dislocation density. CHN analysis was carried-out to confirm the presence of L-threonine in the grown crystals. UV-Vis-NIR analysis reveals that LTTU has lesser absorbance in the entire visible and IR region, which is very important for materials possessing nonlinear optical properties. The UV cut-off wavelength for the pure and LT doped thiourea crystals are found to be 295 nm. The bonding structure and molecular associations due to chemical reactions were analysed and also the functional groups present in the crystals were confirmed from FTIR spectroscopy. Microhardness studies were carried out on the crystal at room temperature using a vicker's microhardness tester for assessing the bond strength of the grown crystals. The etch pits can be attributed to the initial dislocations formed at low angle boundaries or segregated impurities. The etch pits did not appear upon continuous etching, suggesting that the pits are due to dislocations which is strongly correlated to the formation of inclusions in the crystals which could have originated from the growth sector boundaries. Second harmonic generation (SHG) of the grown crystals was tested by Kurtz-Perry powder technique using a Nd:YAG laser, which reveals that the second harmonic generation efficiency of the LTTU was comparable to pure KDP.

Chapter V reveals the outcomes of the present investigations along with the scope for the future work.

A list of references has been presented at the end of the thesis.